

Methods of Extraction of Precious Metals from High Carbon Rock

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Abstract

Manifestations of regional ugle-rodizatsii in the etamorphicc-omplex are Riphean age of the northern part of Khankaisky terrane. Using various methods of physicochemical analysis reveals elevated concentrations (10⁻⁴-10⁻⁶ wt.%) of gold and platinum group elements (PGE) in all petrographic varieties of rocks of this complex. According to x-ray fluorescence analysis of described a wide range of geochemically different types of rare and trace elements: Ti, V, Ni, Cr, Pt, Pd, Re, Rh, Os, Ir, Cu, Hg and Au, Ag, Ta, Nb, Sr, Rb, Zr, La, W, Sn, Pb, Zn has been distinguished. In this connection, the development of technique of extracting of gold and platinum group metals from high-carbon rock off the Khankaisky area, is very important.

Keywords

Geology; High-carbon ROCK; Gold; Platinum; Recovery

Introduction

Many researchers assign the high-carbon stratified metamorphic rocks to one of the main sources of growth of the reserves of gold and platinum group metals in Russia and China in the XXI century. Among these objects is the regional graphitization zone in the North Khanka terrane elongating along the Russian Federation and the People's Republic of China boundary as a submeridional band more than 100 km long and 3 to 5 km wide.

The deposit of crystalline graphite of the Tamgin-Turgenevskaya group (Primorsky Krai), accumulating significant reserves of gold and platinum-group metals, is chosen as the base object for investigations [1]. The largest deposits of this area are the Tamginskoe (center) and Turgenevskoe (south flank) deposits where the stone materials have been sampled for investigations.

Geological Structure

Biotite-feldspar-graphite, garnet-biotite-feldspar-graphite,

and biotite-muscovite-feldspar shales alternated with graphite-bearing garnet-diopside skarns and conformable injections of the graphitized biotite and leucocratic granite-gneisses participate in the geological structure of these deposits. Along with these rocks, small stocks of the late rare-earth granites as well as thin quartz veins and veinlets are also found. The most significant economical gold concentrations (3-22 g/t) are related with the endogenous carbonization, skarns, and quartz hydrothermalites.

Ore mineralization associated with graphite shows rather complicated polymineral composition and diverse forms of precious metal occurrence – native elements, solid solutions, and intermetallic compounds. Free gold occurs as particles of an irregular form, laminated segregations, and not rare gold flakes of spheroidal contour. The range of the granulometric scale, comprising the visible gold classes, is not large (70-100 mkm). Chemical composition of the metal varies within comparatively narrow limits: content of the main admixture – Ag usually does not exceed 6-8 mass % testifying to the gold high fineness. Among other microelements, copper is found in amounts of 2-3 mass %. In the gold flake, containing microinclusions of carbonaceous matter, concentration of Au varies from 93.3 to 97.9 mass % and Ag – from 2.1 to 3.5 mass %. In other survey sites of the same particle, Ag is absent, and Cu is 2.1 mass %. In addition, the sites with 100 % Au content are found. Non-uniformity of gold composition within a single grain is, probably, for its crystallization from a gas phase.

Segregations of the natural mercuric gold with Au concentrations of 90.88 at. % and Hg – 9.12 at. % are rather widespread. The segregations are about 1-2 mkm in size. Some researchers believe that the Hg-bearing mineralization is related from deep-seated fluid. Sometimes, the micron segregations of Au-Cu

intermetallic compounds are found. The composition of these phases (Au – 65.9 at. % and Cu – 34.1 at. %) is close to the formula of cuproauride - CuAu_3 .

Rare findings are small grains of intermetallids of gold, silver, palladium, and tin revealed through the graphite ore thermal oxidation. Their chemical composition (without matrix background) is (mass %): Au – 24.5; Ag – 10.53; Pd – 58.1; Sn – 6.87.

The main barrier on the way of elaboration of the analysis methods and concentration of PM from the stated raw material is the presence of carboniferous matter.

To develop the graphite objects, it is necessary to create the ecologically pure low-waste technology of the mineral raw material processing with the maximal extraction of useful components and, first of all, graphite, gold, and platinum-group metals (PGM).

Carbon-bearing gold concentrates belong to the resistant raw material, particularly, due to big losses of reagents caused by the sorption of the latter [2] that require special chemical methods of processing. Interesting is the study of a possibility of extraction of useful components from graphite ore and special features of gold distribution in the process of a preliminary concentration stage and on different stages of chemical treatment of graphite-bearing rocks.

Method of Analysis of Precious Metals

Problems of reliable determination of gold and PGM in graphite-bearing rocks result from the fact that the carbon matter in them is represented by graphite, which makes their decomposition rather difficult [3]. So to determine gold concentration, we propose a method of instrumental neutron-activation analysis with the use of the Californian source of neutrons (NAA), whose sensitivity is controlled only by nuclear-physical properties of elements.

We have established a dependence of the analysis reliability degree on the sample weight and gold concentration in it. Determination of an optimal weight of the study sample (300 g) withdraws the question about the sample representative. It turned out that only high concentrations of fine gold (more than 200 g/t) markedly influence the analysis error. It is connected with the rise of “self-screening” effect, when a part of the neutron stream is consumed with the surface layers that results in the increase of the inner layer activation. In the analysis of samples with dispersive gold concentration of less than 200 g/t, this

effect is insignificant. However, there are other factors that may influence the errors of determination of gold. The studied ores contain abundant carbon which is an effective inhibitor of neutrons because of a high scattering cross-section. So the presence of carbon in the rock may theoretically influence the results of NAA. To check this suggestion, we have done the neutron-activation determination of gold from samples up to 300 g with a variable carbon concentration. Influence of carbon on the NAA resulting in the experiment run has not been detected. These observations were supported by the data obtained in the experiments on determination of neutron streams for silicate and graphite-bearing samples are with total mass of the charged rock of about 3 kg. Influence of carbon on neutron streams was not fixed in this case. Consequently, the NAA is the most reliable method to study the gold distribution in high-carbon rocks.

Extraction of Useful Components.

A big-volume sample of the graphitized granite-gneisses of Turgenevskoe deposit was taken to be studied. Using the NAA we have found low contents of Au in it (on the verge of the instrument sensitivity limit), that made us resort to the flotation concentration of material.

The study samples were crushed to a size of 0.044 mm and then were floated on the laboratory flotation machine at one stage during 10-30 minutes. Pine oil was used as a frothing agent, and long-chain amine – as a collector.

The bulk of graphite (~ 90 %) and a portion of quartz under these conditions of floatation were concentrated in the froth product. According to the NAA data, the froth product didn't contain any gold, and Au concentration in the chamber product was 2 g/t. To extract and concentrate gold, we subjected the chamber product to floatation with ammonium hydrodifluoride and studied the gold distribution between phases at different stages of hydrodifluoride processing.

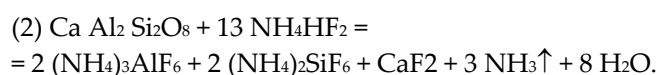
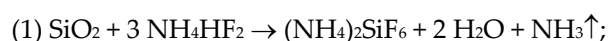
The scheme of ore processing with ammonium hydrodifluoride is based on the physical-chemical properties of ammonium fluorine-metallates [4, 5] that are formed with ore stripping, separated due to different volatility or solubility, and transformed by water vapor to oxides. Gold and other precious metals don't interact with ammonium hydrodifluoride.

The floatation chamber product is dominated by

microscopic (70-100 mkm) gold flakes with laminated and spheroid contours that in many cases associated with clay minerals and silicates. The presence of other native metals (aluminum, iron, copper, etc.), in addition to gold in graphite-bearing rocks of Turgenevskoe deposit testifies to sulfur low activity at the first stage of mineral formation and poor development of sulfidization processes within Turgenevskoe deposit. X-ray analysis shows that the floatation chamber product is composed mainly of two minerals – quartz SiO_2 and anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$.

Aluminosilicates of natural origin, that don't contain hydroxyl and crystallization water, are, as a rule, refractory, thermally stable, and not soluble in water. They always can be decomposed by hydrofluoric acid, and the interaction with ammonium hydrodifluoride depends on their structures. However, inosilicates, nesosilicates, layered and banded silicates, and hydromica, having a compound chemical composition, react with NH_4HF_2 even through being blended.

Thus, the process of fluorination with ammonium hydrodifluoride of the main components of the floatation chamber product of graphite-bearing rock of Turgenevskoe deposit can be shown by the equations as follows:



Ammonium hexafluorsilicate $(\text{NH}_4)_2\text{SiF}_6$ is a ready volatile compound, which through heating can be transformed to a gas phase at 300-350°C, and through cooling can be sublimated at 200°C. Ammonium hexafluoraluminate $(\text{NH}_4)_3\text{AlF}_6$, formed through fluorination with a silicate component, is solved in water. During heating it undergoes thermal decomposition with emanation of ammonia and fluoric hydrogen, that is transformed to a gas phase, and after falling into a cool condenser (room temperature) they combine into NH_4F . High temperatures of evaporation of aluminum fluorides, iron, and calcium create the conditions for deep separation of volatile (silicon) and non-volatile (aluminum, calcium, admixture of iron, etc.) fluorides which form slime and in which gold and other platinum group metals are concentrated.

It should be noted that the ammonia hexafluoraluminate $(\text{NH}_4)_3\text{AlF}_6$ that is formed through fluorination of a silicate component is a semifinished item in the production of aluminum fluoride. And ammonia

hexafluorsilicate $(\text{NH}_4)_2\text{SiF}_6$ is widely used in the production of the amorphous silicon dioxide of high purity that contributes to maximal extraction of useful components from graphite-bearing ore of Turgenevskoe deposit and to creat of low-waste technology of processing of graphite-bearing gold-containing ore by the ammonia hydrodifluoride.

The floatation chamber product was mixed with NH_4HF_2 in a mass ratio of 1:2.3 and heated to 450°C at a rate of 2 degrees a minute. This operation resulted in the fluorination of the main ore components by the ammonia hydrodifluoride with the formation of fluorammonia salts, thermal decomposition of fluorammonia salts of aluminum and iron, and transformation of fluoric ammonia and ammonia hexafluorsilicate into a gas phase. After this treatment, gold was concentrated in the non-volatile residuum whose mass was about 50 % of the original sample mass.

As a result, "dry" stripping of graphite-bearing gold-containing ore by the ammonia hydrodifluoride increases the concentration of the metal being extracted two times. Greater concentration of gold can be achieved by the combination of dry stripping and hydrometallurgical processing of the product. Such the expedient allows the fluorides of aluminum and iron to be transformed to soluble ammonia fluormetallates and to be removed with washing. In this case, after the sample dissolution, total gold is concentrated in the insoluble sediment.

X-ray-phase analysis showed that the non-volatile residuum, obtained at 450°C heating, contained bad-soluble compounds of aluminum and iron - NH_4AlF_4 , AlF_3 , и FeF_3 .

To transform them to a soluble form we carried out the repeated fluorination by the ammonia hydrodifluoride at 200°C and leached with water the resulted fluorammonia salts of aluminum and iron. This treatment resulted in the concentration of gold in the soluble residuum which was a viscous product of yellow color, and its mass was ~12 % of the original sample mass. Au content in the insoluble sediment was 21 g/t.

Processing of the insoluble sediment with hydrofluoric acid makes it possible to obtain a dry product of grey color, in which one can see isolated fragments of native gold 200-450 mkm in size. Microphotos of these particles have been done with the optical confocal scanning microscope of Lext mark are given in the Figure 1.

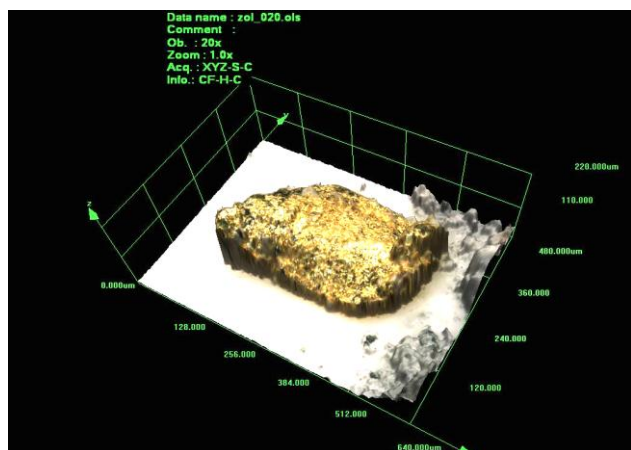


FIG. 1. ASM-IMAGE OF AN ISOLATED FRAGMENT OF NATIVE GOLD OBTAINED THROUGH PROCESSING OF THE GRAPHITE-BEARING GOLD-CONTAINING ORE BY AMMONIA HYDRODIFLUORIDE

Conclusions

Thus, the use of the expedients of the hydrodifluoride processing when stripping the gold-containing graphite-bearing rocks makes it possible not only to concentrate gold, but also to extract the accompanying useful components as the products widely used in the chemical production. This will contribute to maximal extraction of useful components and to creating the resource-saving technology for the processing of this kind of the solid mineral raw material. The elaborated modes of PM extraction open the ways to develop the resource-saving technological scheme of utilization of high-carbon technogenic raw material.

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REFERENCES

- Khanchuk A.I., Plyusnina L.P., Molchanov V.P. Original data on gold-platinoid mineralization in carbonaceous rocks of Khanka massif and prediction of a large deposit of precious metals in Primorsky Krai // *Doklady Akademii Nauk* (Reports of Russian Acad. Sci.). 2004. V. 397, N 4. P. 524-529.
- Khanchuk A.I., Plyusnina L.P., Molchanov V.P., and others. Precious metals in high-carbon metamorphic rocks of Khanka terrane, Primorye // *Tikhookeanskaya Geologiya* (Pacific Geology). 2007. V. 26. N 1. P. 70-80.
- Meretukov M.A., Orlov A.M. Metallurgy of precious metals. Foreign experience. Moscow: "Metallurgy". 1991. 415 pp.
- Patent of the Russian Federation N 2120487, MKI⁶ C22 B 11/00. Mode of the processing of gold-bearing raw material // Mel'nichenko E.I., Moiseenko V.G., Sergienko V.I., Epov D.G., Rimkevich V.S., Krysenko G.F.
- Rakov E.G. Ammonia fluorides. Totals of science and technique. Inorganic chemistry. V. 15. Moscow: INITI, 1988, 154 pp.